A Self-Consistent Atomic Deformation Method for Application of Density Functional Theory

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We employ density functional theory using a method which expresses the total electronic density as a sum over "atomic" densities. The "atomic" denisties are determined self-consistently from a variational treatment of the total energy, which includes terms to account for kinetic energy due to the overlapping densities from separate atomic sites.

I. INTRODUCTION

Following the development of the Thomas-Fermi-Dirac statistical method, the electronic density, rather than the wave function, often has been used as the basic variable for expressing the energy of a collection of atoms. In early applications of this density functional approach, the total density was simply assumed to be the sum of the densities of the separate atoms.[1] This approch provided a qualitative description of atomic forces which guided the development of empirical models. A major advance was provided by Gordon and Kim[2] (GK) who showed that remarkablly good quantitative results could be achieved for closed shell systems by carefully evaluating the "electron gas" expressions using free atom densities.

A few years before the GK work Hohenberg and Kohn[3] proved that the ground state energy of a system of electrons was uniquely expressed as a functional of the density regardless of the external potential. This remarkable result added credibility to the density functional approach, although it evidently was not a motivating factor for the GK work. Soon after the Hohenberg-Kohn theorem was published Kohn and Sham[4] (KS) proposed a variational method for applying the density functional approach. In this method the density of an N electron system is given by the sum of the squares of the N lowest energy self-consistent solutions of an effective one-electron Schrödinger's equation whose potential is defined, variationally, to minimize the total energy. The many calculations of total energy, beginning with those of Janak et. al.[5] (ten years after the KS work and 4 years after that of GK), have established the highly successful field known today as density functional theory.

In this paper we describe a computational method for applying density functional theory using a KS-like variational proceedure with the density expressed as a sum over atomic-like densities. The method, which we call self-consistent atomic deformation (SCAD), can be viewed also as an extension of the GK-model which allows complete relaxation of the atomic densities. This approach is taken also in the work of Cortona[6], but with applications limited to densities expressed as overlapping spherical atoms. In the SCAD method the atomic densities are allowed to have nonspherical deformations. Other self-consistent atomic models can be found in the works of Muhlhausen and Gordon[7], LaSar[8], Bukowinski and coworkers[9] and Edwardson[10]. Francisco et. al.[11] include self-consistency in an atomic model that orthogonalizes the orbitals of an atom with those of its neighbors to obtain spherical densities and pair potentials following the GK method. The direct energy minimization technique of Lacks and Gordon[12], which accounts for nonspherical ions by incorporating spherical bonding charges between spherical ions, has been quite successful in treating various oxides.

Our SCAD method evolved from an effort to extend the potential induced breathing model[13] to handle nonspherical ions, a feature known to be essential for treating oxide ferroelectrics[14]. Ivanov and Maksimov[15] have developed a closely related approach to deal with nonspherical ions, including those in oxide ferroelectrics. We were motivated substantially by Edwardson's work together with a general effort to develop first principles methods for ferroelectric materials[16]. We have preveously given brief discussions of the SCAD model[17–20] which includes some applications of the SCAD for spherically symmetric ions (SSCAD). A detailed description of the SSCAD method is given by Stokes et. al.[21], for which computer code is available. It has been applied in a cluster expansion technique to compute the MgO-CaO phase diagram.[22] Our first application of SCAD for nonspherical atoms was to compute Born effective charges, the quantities that give the change in polarization resulting produced by structural distortions, for ferroelectric oxides and alkaline earth oxides.[23] It has been argued[24] that the calculation of polarization using overlapping atomic-like densities, or Clausius-Mossetti type models, is fun-

damentally flawed. However, the argument is based on a false assumption about the way polarization is computed in such models.[25] Reasonable results have been obtained for polarization and related properties for a variety of compounds using the SCAD method.[26–29]

II. THE SCAD MODEL

Following Hohenberg and Kohn[3] we write the total energy E as a functional of the electronic density n:

$$E[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{es}[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] \ ; \qquad (1)$$

where T is the kinetic energy, E_{es} is the electrostatic energy and E_{xc} is the exchange and correlation energy. We write the total density as a sum of atomic-like densities,

$$n(\mathbf{r}) = \sum_i n_i(\mathbf{r} - \mathbf{R}_i) \qquad (2)$$

centered at $\mathbf{R}_i$. Each atomic-like density is expressed as a spherical harmonic expansion about an origin at its nucleus,

$$n_i(\mathbf{r}) = \sum_{l,m} n^{(i)}_{l,m}(r) Y_{l,m}(\hat{\mathbf{r}}). \qquad (3)$$

To this point we have not made any approximation since the form of the charge density imposes no constraints. In other words, assuming we know the functionals in Eq.(1), the formulation for density is sufficiently general to determine the absolute minimum of E. Of course, we do not know T or E_{xc} exactly. The calculations reported here use the local approximation for E_{xc} given by Hedin and Lundqvist[32]. The kinetic energy is approximated by

$$T[n(\mathbf{r})] = \sum_i T_0[n_i(\mathbf{r})] + T_k[n(\mathbf{r})] - \sum_i T_k[n_i(\mathbf{r})], \quad (4)$$

where $T_0[n_i(\mathbf{r})]$ is the kinetic energy of non-interacting electrons centered about the site i and T_k is a functional to account for additional kinetic energy due to the overlapping of densities from neighboring sites. The density, n_i, is determined from the solutions of a one electron Schrödinger's equation for site i with a potential

$$v_i(\mathbf{r}) = v_{es}[n(\mathbf{r})] + v_{xc}[n(\mathbf{r})] + v_k[n(\mathbf{r})] - v_k[n_i(\mathbf{r})] \ , \quad (5)$$

derived variationally from the total energy.[20] Here, v_{es} is the electrostatic potential due to the atomic nuclei as well as the electron density and v_k (v_{xc}) denotes the functional derivative of T_k (E_{xc}) with respect to density. To compute n_i from v_i we first express v_i in terms of spherical harmonics,

$$v_i(\mathbf{r}) = \sum_{l,m} v^{(i)}_{l,m}(r) Y_{l,m}(\hat{\mathbf{r}}), \qquad (6)$$

and then solve the ith Schrödinger's equation. The details involved in these two steps are described in the next two sections.

The self-consistent solution for v_i (and hence, n_i and n), obtained by occupying the lowest one electron energy levels for the entire system, allowing for charge transfer when indicated, minimizes the total energy in accord with Janak's theorem[30]. This is demonstrated with results for the SSCAD model[21,23] and with results for the SCAD model in section??.

The caluclations presented in this paper use the local Thomas-Fermi form for the overlap contribution to the kinetic energy:

$$T_{TF} = A \int n^{5/3}(\mathbf{r}) d\mathbf{r} \qquad (7)$$

where

$$A = \pi^{4/3} 3^{5/3}/10 \qquad (8)$$

(Hartree atomic units are used throughout this paper.) We have also examined nonlocal functionals of the form

$$T_k = \alpha T_{TF} + \beta \int \frac{|\ \nabla n(\mathbf{r})\ |^2}{n} d\mathbf{r} \qquad (9)$$

and

$$T_k = A \int n^{5/3}(\mathbf{r}) F[s(\mathbf{r})] d\mathbf{r} \qquad (10)$$

where

$$s(\mathbf{r}) = \frac{|\ \nabla n(\mathbf{r})\ |}{2 n(\mathbf{r}) k_f(\mathbf{r})} \qquad (11)$$

and k_f, the local Fermi wave vector, is given by

$$k_f(\mathbf{r}) = (3\pi^2 n(\mathbf{r}))^{1/3}. \qquad (12)$$

For completeness and possible future use in the SCAD method, derivation of the potentials corresponding to the above expressions for T_k are presented in appendix A. Lacks and Gordon[33] have studied several kinetic energy functionals with these forms by comparing with Hartree-Fock calculations for He and Ne atom pairs.

The proceedure for obtaining a self consistent solution for the total energy is easly stated. 1) Atomic-like denisites are used to compute potentials at each site using Eq.(5). 2) New densities are obtained from the solutions of the corresponding one-electron Schrödinger equations. Steps 1 and 2 are repeated, with optimal mixing of old and new densities, until convergence is achieved. In the final step (3) the total energy is determined from the converged potentials and densities. In practice, there are many details to be considered in each step. These are presented and discussed below in three corresponding sections.

There are, of course, certain numerical techniques that are common to all three steps (sections). For example,

we represent both charge densities and potentials as a sum over radial functions times spherical harmonics, a functional form that results naturally from the method we choose for solving the one-electron Schrödinger equations. Presentation of details common to more than one section are done sequentially, with appropriate references to the other sections.

III. CALCULATION OF THE POTENTIAL

In this section we address the following problem: Given charge densities on each site i, expressed as in Eq.(3), determine similarly expressed potentials (Eq.(6)). The radial dependences of $n^{(i)}_{l,m}(r)$, $v^{(i)}_{l,m}(r)$ and similar functions are kept on a mesh that starts a $r = 0$ and has separations between points that increase logarithmically. A detailed discussion of the mesh and related integration, interpolation etc. is offered in appendix B.

First of all, we add and subtract the term $v_{xc}[n_i(\mathbf{r})]$ to the potential (Eq. 5),

$$v_i(\mathbf{r}) = v_{es}[n(\mathbf{r})] + v_{xc}[n_i(\mathbf{r})] + v_{ov}[n(\mathbf{r})] - v_{ov}[n_i(\mathbf{r})], \tag{13}$$

where $v_{ov} = v_k + v_{xc}$.

The electrostatic potential includes contributions from the nuclear charge as well as the electronic density and, unless the net moments of charge for $l \leq 2$ happen to be zero, it is long ranged in nature; which is to say that contributions from all atoms in the system must be included. The electrostatic potential can be expressed as a linear superposition of the corresponding potentials of each "atom", or from any other way we want to partition the charge density. On the other hand, the overlap potential is a nonlinear function of the density, and therefore cannot be so decomposed. Fortunately, it is short ranged and can be decomposed into a part that is smooth (compared to the behavior of the density in the vicinity of an atomic nucleus) and a part which, by design, is linear. The smooth part, along with other smooth parts, discussed below, and collectively called v_s, are computed on a 3 dimensional grid with a relatively coarse radial mesh and an angular grid chosen for efficient integration[35].

Let R_c be a cut-off radius within which the densities of atom pairs have appreciable overlap. The potential due to atoms farther than R_c from the ith site are included using expressions for point poles. Contributions from monopoles, dipoles and quadrupoles are computed using the Ewald method while contributions from $l > 2$ poles are included in a similar manner with direct-scace sums only (Appendix C). To account for the electrostatic potential due to near neighbors, with separations $\mid \mathbf{R}_i - \mathbf{R}_j \mid < R_c$, one could "simply" transform the $Y_{l,m}$ expansions of $v^{(j)}_{es}$ to similar expansions about an origin at the ith site. The method for changing the origin of a shperical harmonic expansion (Löwdin transformation) is discussed in appendix D. In fact, we include only the $l = 0$ portion of the jth electrostatic potential using the Löwdin technique and include the $l > 0$ contributions, which are relatively smooth near the atomic nuclei, in v_s.

A smooth part of the overlap potential is created by adding and subtracting the term $\sum_j{}' v_{ov}[n^{(j)}_0(\mathbf{r})]$, where n_0 denotes the $l = 0$ portion of the density and the prime on the summation indicates the j=i term is omitted. The subrtacted term combines with the last two terms of Eq.13 to give the smooth overlap contribution included in v_s. The added term is included, along with the $l = 0$ part of the electrostatic potential from near neighbors, using the Löwdin transformation.

The nonspherical part of the onsite exchange-correlation potential, defined by $v_{xc}[n_i(\mathbf{r})] - v_{xc}[n^{(i)}_0]$ is also smoothly varying, owing to the fact that the density becomes spherical near the nucleus. Therefore, it is conveniently included in v_s as well.

To summarize, the potential for the ith atom is decomposed, for computational purposes, as follows:

$$v_i(\mathbf{r}) = v^{(i)}_{on}(\mathbf{r}) + v^{(i)}_s(\mathbf{r}) + v^{(i)}_L(\mathbf{r}) + v^{(i)}_p(\mathbf{r}) + v^{(i)}_n(\mathbf{r}); \tag{14}$$

where each term, with subscripts denoting onsite, smooth, Löwdin, poles (outside R_c) and nuclear. The onsite nuclear part is included in v_{on} while nuclear contributions from far neighbors are included in v_p.

The onsite term is the sum of the radial exchange-correlation term (introduced above to create a contribution to the smooth term) and the electrostatic potential due to the onsite electrons and the nuclear charge with atomic number Z_i.

$$v^{(i)}_{on}(\mathbf{r}) = v_{xc}[n^{(i)}_0(r)] + \int \frac{n_i(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} d\mathbf{r}' - \frac{Z_i}{r}. \tag{15}$$

Substituting the expanded forms of n_i (Eq.3) and $\mid \mathbf{r} - \mathbf{r}' \mid^{-1}$ (addition theorem), the angular integrations are trivially performed to give

$$v^{(i;l,m)}_{on}(r) = \delta_{l0}\left(v_{xc}[n^{(i)}_0(r)] - \frac{\sqrt{4\pi}Z_i}{r}\right) + r^{-(l+1)}G^{(i)}_{l,m}(r) + r^l H^{(i)}_{l,m}(r) \tag{16}$$

where

$$G_{l,m}(r) = \frac{4\pi}{(2l+1)}\int_0^r x^{(l+2)} n^{(i)}_{l,m}(x)dx \tag{17}$$

and

$$H_{l,m}(r) = \frac{4\pi}{(2l+1)}\int_r^\infty x^{(1-l)} n^{(i)}_{l,m}(x)dx \tag{18}$$

The radial integrations are carried out as described in appendix B. The values of $G^{(i)}_{l,m}(\infty)$ give the multipole moments that enter $v^{(i)}_p$ (see appendix C).

The smooth potential

$$v_s^{(i)}(\mathbf{r}) = v_{xc}[n_i(\mathbf{r})] - v_{xc}[n_0^{(i)}(r)] + v_{ov}[n(\mathbf{r})] - v_{ov}[n_i(\mathbf{r})] - \sum_j{}' v_{ov}[n_0^{(j)}(\mathbf{r})] + \sum_j{}' \Big(v_{es}[n_j(\mathbf{r})] - v_{es}[n_0^{(j)}(\mathbf{r})]\Big) \quad (19)$$

is computed by accumulating values for the required densities and v_{es} on the course mesh centered at the i site. This is the most time consuming part of the calculation. For every neighbor j the values of each radial function of the spherical harmonic expansions must be determined by interpolation and the corresponding values of $Y_{l,m}(\mathbf{r}-\mathbf{R}_j)$ computed as well. Once values of $v_s^{(i)}(\mathbf{r})$ are determined on the course radial mesh, the coefficients of the spherical harmonic expansion are determined by numerical integration over solid angle Ω.

$$v_s^{(i;l,m)}(r) = \int v_s^{(i)}(\mathbf{r}) Y_{l,m}^*(\hat{\mathbf{r}}) d\Omega \quad (20)$$

The resultant functions of r are then interpolated from the course to the dense radial mesh.

The spherical harmonic expansion of the Löwdin potential

$$v_L^{(i)}(\mathbf{r}) = \sum_j{}' \Big(v_{ov}[n_0^{(j)}(\mathbf{r})] + v_{es}[n_0^{(j)}(\mathbf{r})]\Big) \quad (21)$$

is computed as described in appendix D. Since it can have sharp features near the neighbors at $\mathbf{R}_j$, additional values are determined in these regions in order to accurately carry out integrations for contributions to the Hamiltonian and total-energy.

Evaluation of the point-pole part of the potential (v_p) requires the multipole moments, i.e., the values of $G_{l,m}^{(i)}(\infty)$, combined with, for monopole terms, the nuclear charges (Z_i). Details of this part of the calculation are discussed in appendix C.

Finally, we include the potential due to neighboring nuclei,

$$v_n^{(i)}(\mathbf{r}) = \sum_j{}' \frac{Z_j}{|\mathbf{r}-\mathbf{R}_j|}, \quad (22)$$

where the sum over j excludes the $j=i$ term and terms with $\mid \mathbf{R}_i - \mathbf{R}_j \mid > R_c$. As already mentioned, contributions from nuclei outside the cut-off sphere are included in the monopole term of $v_p^{(i)}$ and the $i=j$ term is included in the onsite potential v_{on}. Spherical harmonic expansions about the ith site are given by the addition theorem.

IV. CALCULATION OF CHARGE DENSITY

The first consideration in calculating the electron density is to choose a set of basis functions for each site for use in solving the Schrödingers' equations for each v_i. A convenient approach, which we have used in previous work, is to select the Slater-type radial functions from published tables[38,39]. However, this approach has limited variational freedom. More recently we have employed other methods for constructing basis functions that remove this limitation. This is discussed further below. In either case, the density used in the first iteration can be obtained from the published tables[38,39] of atomic orbitals.

To illustrate the method for solving the Schrödingers' equations for each site, assume a set of Slater-type functions are given (for each site) to build a basis set for expanding the wave functions at each site. In subsequent discussion we drop the site index. Slater functions have the form $r^{n_s}e^{-\beta_s r}$ where n_s are integers ($n_s \geq 0$) and values for β_s range from ~ 1 to a few tens, depending on the atom. The larger values of β_s are needed for heavier atoms to give an accurate representation of the inner core levels. Likewise, we need radial mesh points nearer the nucleus for the heavier atoms. For convenience, we determine the first mesh point from the maximum value of β ($r_1 = g/(2\beta_{max})$). See Appencix B for detail.

The tabulated Slater functions are associated with particular angular momenta l_s. We define a minimal basis set from the radial functions times spherical harmonics $Y_{l_s m}(\hat{\mathbf{r}})$. An extended basis can be created that allows for greater angular variation by multiplying the radial functions by $Y_{lm}(\hat{\mathbf{r}})$ with $l > l_s$. Thus, in general, the basis functions are given by

$$\phi_i(\mathbf{r}) = r^{n_s}e^{-\beta_s r}Y_{lm}(\hat{\mathbf{r}}) \qquad (l_{max} \geq l \geq l_s). \quad (23)$$

Strictly speaking, l_{max} should not be greater than n_s to avoid having unphysical results for the wave function at the origin. In practice, this does not introduce noticeable error in the total energy provided $l_{max} \leq n_s+2$, evidently because of the r^2 factor that enters the integrations over volume. If higher l's are needed then radial functions for correspondingly higher n_s should be generated to cover an equivalent range of radii. This is discussed in greater detail below in the presentation of methos for systematically increasing the variational freedom.

Schrödinger's equation for a given atomic site is solved in terms of the basis functions ϕ_i. The proceedure is straight-forward and well known, so we do not go through it in detail here. Instead, we give a brief discussion of the method with enough detail to emphasize aspects of the problem that are relevant for implimenting the SCAD model.

The expansion coeficients (c_j) for a wave function $\psi(\mathbf{r}) = \sum_j c_j\phi_j(\mathbf{r})$ are determined by solving the matrix equation

$$(\mathbf{H} - \epsilon\mathbf{S})\mathbf{c} = 0 \quad (24)$$

where

$$H_{ij} = \int \phi_i^*[-\frac{1}{2}\nabla^2 + v(\mathbf{r})]\phi_j(\mathbf{r})d^3r, \quad (25)$$

$$S_{ij} = \int \phi_i^* \phi_j(\mathbf{r}) d^3r \tag{26}$$

are the elements of the overlap matrix **S** and **c** denotes the array of expansion coeficients.

Depending on the particular atom and the number and choice of additional basis functions included beyond the minimal set, some eigenvalues of **S** may be quite small. This indicates that **S** is nearly singular and could imply that the additional functions were not very carefully selected. If this is the case, numerical noise can result in the total energy as a function of structural distortion if nearly linearly dependent combinations of basis functions are included in the representation of the wave function. This problem is automatically avoided by transforming to an orthogonal basis which excludes the space corresponding to eigenvectors of **S** with "small" eigenvalues. The calculations we have carried out so far indicate that a reasonable definition of "small" to be ~ 0.0001. We refer to this cut-off value as the basis optimization parameter (BOP) because we want it to be as small as possible to give the maximum variational freedom allowed by the basis functions without producing noisy results.

Evaluation of the matrix elements is straight forward. The kinetic energy operator in spherical coordinates separates into the familiar radial and angular momentum operators. Integrations for fixed radius are given by the well known "3-j" coefficients. Radial integrations are carried out as discussed in Appendix B. If Slater-type basis functions are used, then radial integrations for contributions from onsite and near-neighbor nuclei take the form $\int r^n e^{-\beta r} dr$. Analytic expressions for such integrals can be used for $n \neq -1$ and simple approximate formulae are available for $n = -1$.[34] However, their use in the SCAD code did not provide any benifit over numerical integrations.

The Hamiltonian matrix for each non-equivalent atom in the unit cell is computed and diagonalized. Then the lowest energy levels for the entire system are occupied by the available electrons. For some systems this may lead to charge trasfer among the atoms to achieve a common highest occupied level and give the minimum total energy. Once the occupation numbers for the energy levels of each atom are determined, the wave functions are squared, weighted by the occupation numbers and summed to get the total density for each atom. The squared wave functions contain procucts of two Y_{lm}'s, which are readily converted into a linear combination of single Y_{lm}'s using appropriate 3-j coefficients. We note that the maximum l in the charge density expansion is two times the maximum l in the wave function.

During the iteration cycles the radial functions in the charge density expression only need to be determined on the logarithmic mesh. Extra points needed for accurate integration over sharp features in $v_L(\mathbf{r})$ are determined for the density at the final iteration to obtain an accurate total energy. Of course, the radial integrations involving the basis functions must be carried out accurately over the structure in v_L in each iteration. The sharp features in v_L are determined at the extra points by interpolation from values for the integrals (given in Appendix D) on the logarithmic mesh.

V. CALCULATION OF TOTAL ENERGY

Straight forward but tedious. Will fill in later as time permits.

Notes to author - Mention values for mesh growth factor. Relate iteration error to total energy precision.

VI. APPENDIX A: KINETIC ENERGY FUNCTIONALS

Lacks and Gordon[33] proposed non-local correction to the Thomas-Fermi kinetic energy functional that have the form of Generalized Gradient Approximation functionals for the exchange-correlation energy. Thus in their approximation, the kinetic energy of an electron gas with density $n(\mathbf{r})$ is given by

$$T[n(\mathbf{r})] = A_k \int d^3r \, n(\mathbf{r})^{5/3} F[s(\mathbf{r})] \ , \tag{27}$$

where for an unpolarized electron gas

$$A_k = \pi^{4/3} 3^{5/3}/5 \tag{28}$$

if the energy is in Rydbergs, and $s(\mathbf{r})$ is a measure of the local non-uniformity of the electron gas:

$$s(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|}{2n(\mathbf{r}) k_f(\mathbf{r})} \ . \tag{29}$$

Here k_f is the local Fermi wavevector:

$$k_f(\mathbf{r}) = (3\pi^2 n(\mathbf{r}))^{1/3} \ , \tag{30}$$

so $s(\mathbf{r})$ is dimensionless. Further, since $s = 0$ for a uniform electron gas, it follows that $F[0] = 1$.

Lacks and Gordon consider only those functions F[s] which are even in s, so we define a new quantity

$$\sigma(\mathbf{r}) = s(\mathbf{r})^2 = \frac{|\nabla n(\mathbf{r})|^2}{4n(\mathbf{r})^2 k_f(\mathbf{r})^2} \ . \tag{31}$$

Since $k_f \propto n^{1/3}$ we can take

$$\sigma(\mathbf{r}) = \alpha n(\mathbf{r})^{-8/3} |\nabla n(\mathbf{r})|^2 \ , \tag{32}$$

where

$$\alpha = (24\pi^2)^{-2/3} \ . \tag{33}$$

Then, writing $F[\sigma]$ in place of $F[s]$, we have

$$T[n(\mathbf{r})] = A_k \int d^3r\, n(\mathbf{r})^{5/3} F[\sigma(\mathbf{r})] \ . \tag{34}$$

Our task is to determine the Kohn-Sham "potential" arising from (34).

We wish to study the change $T[n] \rightarrow T[n] + \delta T[n]$ as we make the change $n \rightarrow n + \delta n$. Keeping only the terms linear in δn we have

$$\begin{aligned} \delta T[n(\mathbf{r})] = \ & A_k \int d^3r\, n(\mathbf{r})^{2/3} \{ \tfrac{5}{3} F[\sigma(\mathbf{r})] \delta n(\mathbf{r}) \\ & + n(\mathbf{r}) F'[\sigma(\mathbf{r})] \delta\sigma(\mathbf{r}) \} + O[(\delta n)^2] \ , \end{aligned} \tag{35}$$

where $\delta\sigma$ is the change in σ as $n \rightarrow n + \delta n$:

$$\begin{aligned} \delta\sigma(\mathbf{r}) = \ & -\tfrac{8}{3} \tfrac{\sigma(\mathbf{r})}{n(\mathbf{r})} \delta n(\mathbf{r}) \\ & + 2\alpha n(\mathbf{r})^{-8/3}\, \nabla n(\mathbf{r}) \cdot \nabla \delta n(\mathbf{r}) + O[(\delta n)^2] \ . \end{aligned} \tag{36}$$

Substituting (36) into (35), and separating the integrals containing δn and $\nabla \delta n$, we find

$$\begin{aligned} \delta T[n(\mathbf{r})] = \ & \tfrac{1}{3} A_k \int d^3r n(\mathbf{r})^{2/3} \{ 5F[\sigma(\mathbf{r})] \\ & - 8\sigma(\mathbf{r}) F'[\sigma(\mathbf{r})] \} \delta n(\mathbf{r}) \\ & + 2\alpha A_k \int d^3r \tfrac{F'[\sigma(\mathbf{r})] \nabla n(\mathbf{r})}{n(\mathbf{r})} \cdot \nabla \delta n(\mathbf{r}) \ . \end{aligned} \tag{37}$$

Applying the divergence theorem to the second line of (37), and noting that integrals over the boundary of a periodically repeated unit cell vanish, we find

$$\begin{aligned} \delta T[n(\mathbf{r})] = \ & \tfrac{1}{3} A_k \int d^3r n(\mathbf{r})^{2/3} \{ 5F[\sigma(\mathbf{r})] \\ & - 8\sigma(\mathbf{r}) F'[\sigma(\mathbf{r})] \} \delta n(\mathbf{r}) \\ & + A_k \int d^3r 2\alpha \tfrac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^2} F'[\sigma(\mathbf{r})] \delta n(\mathbf{r}) \qquad (38) \\ & - 2\alpha A_k \int d^3r \{ F'[\sigma(\mathbf{r})] \tfrac{\nabla^2 n(\mathbf{r})}{n(\mathbf{r})} \\ & + F''[\sigma(\mathbf{r})] \tfrac{\nabla n(\mathbf{r}) \cdot \nabla \sigma(\mathbf{r})}{n(\mathbf{r})} \} \delta n(\mathbf{r}) \ . \qquad (39) \end{aligned}$$

Using (32) on the second line of (39), we obtain the final expression

$$\begin{aligned} \delta T[n(\mathbf{r})] = \ & A_k \int d^3r \delta n(\mathbf{r}) \left(\tfrac{1}{3} n(\mathbf{r})^{2/3} \{ 5F[\sigma(\mathbf{r})] \right. \\ & - 2\sigma(\mathbf{r}) F'[\sigma(\mathbf{r})] \} - 2\alpha F'[\sigma(\mathbf{r})] \tfrac{\nabla^2 n(\mathbf{r})}{n(\mathbf{r})} \\ & \left. -2\alpha F''[\sigma(\mathbf{r})] \tfrac{\nabla n(\mathbf{r}) \cdot \nabla \sigma(\mathbf{r})}{n(\mathbf{r})} \right) \ . \end{aligned} \tag{40}$$

The Kohn-Sham potential is related to its functional by the functional derivative,

$$v_T(\mathbf{r}) = \frac{\delta T[n(\mathbf{r})]}{\delta n(\mathbf{r})} \ , \tag{41}$$

so from (40) we find

$$\begin{aligned} v_T(\mathbf{r}) = \ & A_k \left(n(\mathbf{r})^{2/3} \{ 5F[\sigma(\mathbf{r})] \right. \\ & - 2\sigma(\mathbf{r}) F'[\sigma(\mathbf{r})] \} / 3 - 2\alpha \{ F'[\sigma(\mathbf{r})] \nabla^2 n(\mathbf{r}) \\ & \left. + F''[\sigma(\mathbf{r})] \nabla n(\mathbf{r}) \cdot \nabla \sigma(\mathbf{r}) \} / n(\mathbf{r}) \right) \ . \end{aligned} \tag{42}$$

VII. APPENDIX B: RADIAL FUNCTIONS

Radial functions are stored on a logarithmic mesh chosed so that the *interval* between points increases exponentially. Specifically, the nth interval is given by

$$r_{n+1} - r_n = r_1 (1 + g)^n \tag{43}$$

where the value of r_1 is selected to be the first nonzero mesh point ($r_0 = 0$) and g is a selected growth factor. Eq.(43) implies

$$r_n = [(1 + g)^n - 1] \frac{r_1}{g} \tag{44}$$

The derivative of r with respect to n,

$$r'_n = ln(1 + g)(1 + g)^n \frac{r_1}{g}, \tag{45}$$

is used to facilitate radial integrations. The usual quadrature weights (assuming r is just a constant times n) are simply multiplied by r'_n. We find that few hundred raial mesh points are sufficient to provide integrated densities to an accuracy of 10^{-7} using Simpson's rule.

The integration of a smooth function of r times one with a discontinuity in its radial derivative must be treated carefully. In the SCAD model, discontinuities appear in the radial derivatives of the potential at values of r corresponding to the positions of neighboring atoms. This results from the lower limit of the Löwdin integrals in Eq.(69). These sharp features in the potential can produce noise in the total energy as a function of structural distortions if integrations are carried out by straight-forward quadrature on a fixed radial mesh. We handle this problem by a proceedure which retains points on a fixed radial mesh and includes extra points that vary with structural distortions. As the total potential for a given atom is accumulated on the fixed mesh, we omit Löwdin contributions for a selected number of points on either side of the corresponding neighbor distances. Then, for each neighbor j, the Löwdin potential is evaluated at radii given by Gaussian quadrature from the beginning of the omitted region to R_j and from R_j to the end of the omitted region. Only a few Gaussian points are needed for accurate integration on either side of R_j. Typically, 20 to 30 neighbors are needed for convergence, so a total of about two hundred extra points are needed to handle the integrations over the sharp features in the potential. This is a small part of the overall calculation.

As mentioned in section III the most computationally intensive part of the calculation is in determing the smooth part of the potential, v_s. This requires evaluation of the densities and nonspherical parts of electrostatic potentials due to neighbors at each point on the course mesh. Typically, an atom may overlap with about 25 neighbors and the course mesh may have $\sim$ 30 radial points for $\sim$ 100 directions. Assuming radial functions

are required up to $l = 4$, this gives a total of over 2 million ($2 \times 15 \times 25 \times 30 \times 100$) interpolations per atom. We use a cubic spline interpolation with our indices taken to be the independent variable. This minimizes the number of operations in each interpolation without any loss of accuracy.

VIII. APPENDIX C: EWALD'S METHOD

Ewald's method provides a rapidly convergent formula for the potential of a lattice of point charges in a uniform compensating background. A good discussion of the method is given by Slater.[36] The method employs linear superposition of two oppositely charged, but otherwise identical, Gaussian densities centered at the sites of the point charges. The negative Gaussian densities combine with the positive point charges to give a rapidly convergent real space sum for their contribution to the potential and the positive Gaussian densities combine with the negative background to give a rapidly convergent Fourier series expansion for their contribution. The potential at $\mathbf{r}$ due to unit point charges at $\mathbf{x}(l) + \mathbf{r}^{'}$, where $\mathbf{x}(l)$ are lattice vectors, in a uniform background is given by

$$v_m(\mathbf{r}, \mathbf{r}^{'}) = \frac{4\pi}{V} {\sum_{\mathbf{Q}}}^{'} \frac{e^{-(Q^2/4\epsilon)}}{Q^2} e^{i\mathbf{Q}\cdot(\mathbf{r}-\mathbf{r}^{'})} + \sum_l \frac{erfc(\mid \mathbf{x}(l) + \mathbf{r} - \mathbf{r}^{'} \mid)\epsilon}{\mid \mathbf{x}(l) + \mathbf{r} - \mathbf{r}^{'} \mid} - \frac{\pi}{V\epsilon^2} \quad (46)$$

where $\mathbf{Q}$ are reciprocal lattice vectors, the prime on the summation over $\mathbf{Q}$ indicates the $\mathbf{Q} = \mathbf{0}$ term is omitted and $erfc$, the complimentary error function, is given by

$$erfc(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-y^2} dy \quad (47)$$

and the last term is a constant of integration needed to make the result independent of the Gaussian parameter ϵ. The value of ϵ can be adjusted to give rapid convergence for both real and reciprocal space sums.

We put the point charges a displacement $\mathbf{r}^{'}$ from the lattice vectors for convenience in deriving expressions for the potential due to point dipoles and quadrupoles. For example, we can place point charges of $\pm q$ at $\mathbf{r}^{'} = \pm\hat{\mathbf{x}}d/2$. The resultant potential at $\mathbf{r}$ is given by $v_m(\mathbf{r}, \hat{\mathbf{x}}d/2) - v_m(\mathbf{r}, -\hat{\mathbf{x}}d/2)$. For small d the lowest order (linear) term in an expansion of the above expression about $\mathbf{r}^{'} = 0$ is the potential due to a lattice of point dipoles. In particular, we find the potential due to a lattice of point dipoles in the α direction is given by

$$v_{d_\alpha}(\mathbf{r}) = \frac{4\pi}{V} {\sum_{\mathbf{Q}}}^{'} \frac{e^{-(Q^2/4\epsilon)}}{Q^2} sin(\mathbf{Q}\cdot\mathbf{r}) Q_\alpha + \sum_l \left(\frac{4\epsilon}{\sqrt{\pi} r^2} e^{-r^2\epsilon^2} + \frac{erfc(r\epsilon)}{r^3} \right) r_\alpha \quad (48)$$

Similarly, the potential due to point quadrupoles is given by the second order term in the expansion of v_m about $\mathbf{r}^{'} = 0$. We obtain

$$v_{q_{\alpha\beta}}(\mathbf{r}) = -\frac{2\pi}{V} {\sum_{\mathbf{Q}}}^{'} \frac{e^{-(Q^2/4\epsilon)}}{Q^2} cos(\mathbf{Q}\cdot\mathbf{r}) Q_\alpha Q_\beta + \frac{r_\alpha r_\beta}{2} \sum_l \left\{ \frac{2\epsilon}{\sqrt{\pi}} \left(\frac{2\epsilon^2}{r^2} + \frac{3}{r^4} \right) e^{-r^2\epsilon^2} + \frac{3erfc(\epsilon r)}{r^3} \right\} - \frac{\delta_{\alpha\beta}}{2} \sum_l \left\{ \frac{2\epsilon}{\sqrt{\pi} r^2} e^{-r^2\epsilon^2} + \frac{erfc(\epsilon r)}{r^3} \right\} \quad (49)$$

Calculations using these expressions for v_d and v_q have been tested against Eq.(46) by modeling collections of point charges that approximate point dipoles and quadrupoles.

For the SCAD calculation we require spherical harmonic expansions of the potentials due to point poles that lie outside the cut-off radius R_c. Thus we must remove, from v_m, v_d and v_q, the contributions from nearby poles with $\mathbf{x}(l) < R_c$. Specifically, these contributions are $1/s$ for monopoles, s_α/s^3 for dipoles and $(3s_\alpha s_\beta - \delta_{\alpha\beta}s^2)/2s^5$ for quadrupoles where $\mathbf{s}$ denotes the separation vector from $\mathbf{x}(l)$ to $\mathbf{r}$. Values for v_m, v_d and v_q, with contributions from nearby poles removed, are determined on an angular grid for some selected value of $r = r_s$. The coefficients of the spherical harmonic expansion are then determined by numerical integration over the surface of the sphere with radius r_s.[35] The radial dependence of v_d and v_q are solutions of Laplace's equation, in our case the r^l solutions. The radial dependence of the monopole potential v_m contains, additionally, a spherically symmetric term $\propto r^2$ that originates from the constant charge background. We remove this contribution before determining the spherical harmonic expansion of v_m. Of course, it necessarily sums to zero when the contributions from all the atoms in the crystal are included. In any case, the coefficients of the various spherical harmonic expansions of point-pole potentials, need only be determined for one value of r_s. A reasonable choice is $r_s \sim 1/2$; large enough to avoid numerical uncertainties that could arise for small r and small enough to limit contributions that would require spherical harmonics with large l for high accuracy. In each iteration the point-pole spherical harmonic expansion coefficients are multiplied by the corresponding computed moments and summed over all atoms in the unit cell to give $v_{lr}^{(i)}$. Specifically,

$$v_{lr}^{(i;l,m)}(r) = r^l \sum_{j,k} c(j,k) v_{pp}^{(l,m)}(j,i,k) \quad (50)$$

where the j index designates $v_{pp} = v_m$, v_{d_1}, v_{d_2}, v_{d_3}, $v_{q_{11}}$, $v_{q_{21}}$, $v_{q_{22}}$, $v_{q_{31}}$, $v_{q_{32}}$ and $v_{q_{33}}$ for $j = 1, \ldots, 10$ respectively, the k index sums over all the atoms in the unit cell and the $c(j,k)$ are given by the multipole moments of each atom k and constants which transform between the Cartesian and spherical harmonic discription. In particular,

$$c(1,k) = \frac{G^{(k)}_{0,0}(\infty)}{2\sqrt{\pi}} - Z_k, \tag{51}$$

$$c(2,k) = -\Re[G^{(k)}_{1,1}(\infty)]\sqrt{8\pi/3} \tag{52}$$

$$c(3,k) = \Im[G^{(k)}_{1,1}(\infty)]\sqrt{8\pi/3} \tag{53}$$

$$c(4,k) = G^{(k)}_{1,0}(\infty)\sqrt{4\pi/3} \tag{54}$$

$$c(5,k) = \Re[G^{(k)}_{2,2}(\infty)]\sqrt{8\pi/15} - G^{(k)}_{2,0}(\infty)\sqrt{4\pi/45} \tag{55}$$

$$c(6,k) = -\Im[G^{(k)}_{2,2}(\infty)]\sqrt{32\pi/15} \tag{56}$$

$$c(7,k) = -\Re[G^{(k)}_{2,2}(\infty)]\sqrt{8\pi/15} - G^{(k)}_{2,0}(\infty)\sqrt{4\pi/45} \tag{57}$$

$$c(8,k) = -\Re[G^{(k)}_{2,1}(\infty)]\sqrt{32\pi/15} \tag{58}$$

$$c(9,k) = \Im[G^{(k)}_{2,1}(\infty)]\sqrt{32\pi/15} \tag{59}$$

$$c(10,k) = G^{(k)}_{2,0}(\infty)\sqrt{16\pi/5} \tag{60}$$

IX. APPENDIX D: LÖWDIN TRANSFORMATION

Given a function expressed as a spherical harmonic expansion, the method for transforming that function to a spherical harmonic expansion about a new origin is known as Löwdin's α-expansion.[37] Here we are interested in expanding a spherically symmetric function, $F(r') = f(r')Y_{0,0}$ in terms of spherical harmonics about a new origin. We use the "prime" to denote coordinates with respect to the "old" origin. The two origins are separated a distance a along the z-axis. In this case, the spherical harominic expansion about the new origin can be written

$$F(\mathbf{r}) = \sum_l g_l(r) Y_{l,0}(\hat{\mathbf{r}}) \tag{61}$$

where

$$g_l(r) = \sqrt{2l+1}\int_0^\pi f(r')P_l(cos\theta)sin(\theta)d\theta \tag{62}$$

and, in terms of the polar angle θ, $r'^2 = r^2 + a^2 - 2arcos(\theta)$. Expressing the integration in terms of the variable r' gives

$$g_l(r) = \frac{\sqrt{2l+1}}{ar}\int_{|a-r|}^{a+r} f(r')P_l\left(\frac{r^2+a^2-r'^2}{2ar}\right)r'dr' \tag{63}$$

For $l \leq 4$ we find

$$g_0(r) = d_0(r)I_0(r), \tag{64}$$

$$g_1(r) = d_1(r)[-I_1(r) + (r^2+a^2)I_0(r)], \tag{65}$$

$$\begin{aligned} g_2(r) = d_2(r)[&\tfrac{3}{2}I_2(r) - 3(r^2+a^2)I_1(r) \\ &+ \tfrac{1}{2}(3r^4+2r^2a^2+3a^4)I_0(r)], \end{aligned} \tag{66}$$

$$\begin{aligned} g_3(r) = \quad d_3(r)[&-\tfrac{5}{2}I_3(r) + \tfrac{15}{2}(r^2+a^2)I_2(r) \\ &- \tfrac{1}{2}(15r^4+18r^2a^2+15a^4)I_1(r) \\ &+ \tfrac{1}{2}(5r^6+3r^4a^2+3r^2a^4+5a^6)I_0(r)], \end{aligned} \tag{67}$$

$$\begin{aligned} g_4(r) = d_4(r)[&\tfrac{35}{8}I_4(r) - \tfrac{35}{2}(r^2+a^2)I_3(r) \\ &+ \tfrac{15}{4}(7r^4+10r^2a^2+7a^4)I_2(r) \\ &- \tfrac{5}{2}(7r^6+9r^4a^2+9r^2a^4+7a^6)I_1(r) \\ &\tfrac{1}{8}(35r^8+20r^6a^2+18r^4a^4+20r^2a^6+35a^8)I_0(r)], \end{aligned} \tag{68}$$

$$I_l(r) = \int_{|a-r|}^{r+a} f(x)x^{2l+1}dx, \tag{69}$$

and

$$d_l(r) = \frac{\sqrt{2l+1}}{(2ar)^{l+1}}, \tag{70}$$

This is an efficient form for g_l because the integrals can be obtained by interpolating from tabulated values of the integral with limits from zero to the radial mesh values. However, for small r this expression for g_l becomes numerically unstable, owing large cancellations that counter the effect of having r^{l+1} in the denominator of d_l. A way around this problem is to expand f in a Taylor series about a. The integrals,

$$I_l(r) = \int_{a-r}^{a+r}\sum_n \frac{f^{(n)}}{n!}(x-a)^n x^{2l+1}dx, \tag{71}$$

where $f^{(n)}$ denotes the nth derivative of f evaluated at a, can then be performed analytically, the resultant polynomials subtituted into the corresponding expressions for g_l and each term with some power of r in the denominator has an expression in its numerator that sums identically to zero. We obtain, after considerable algebra, the following expressions for g_l when f is expanded to 4th order:

$$\begin{aligned} g_0(r) = f^{(0)} &+ \tfrac{r^2}{3a}f^{(1)} + \tfrac{r^2}{6}f^{(2)} \\ &+ \tfrac{r^4}{30a}f^{(3)} + \tfrac{r^4}{120}f^{(4)}, \end{aligned} \tag{72}$$

$$g_1(r) = \sqrt{3}[(\frac{r^3}{15a^2} - \frac{r}{3})f^{(1)} - \frac{r^3}{15a}f^{(2)} + (\frac{r^5}{210a^2} - \frac{r^3}{30})f^{(3)} - \frac{r^5}{210a}f^{(4)}], \quad (73)$$

$$g_2(r) = \sqrt{5}[(\frac{r^4}{35a^3} - \frac{r^2}{15a})f^{(1)} - (\frac{r^4}{35a^2} - \frac{r^2}{15})f^{(2)} + (\frac{r^6}{630a^3} + \frac{r^4}{210a})f^{(3)} - (\frac{r^6}{630a^2} - \frac{r^4}{210})f^{(4)}], \quad (74)$$

$$g_3(r) = \sqrt{7}[(\frac{r^5}{63a^4} - \frac{r^3}{35a^2})f^{(1)} - (\frac{r^5}{63a^3} - \frac{r^3}{35a})f^{(2)} + (\frac{r^7}{1386a^4} + \frac{r^5}{210a^2} - \frac{r^3}{105})f^{(3)} - (\frac{r^7}{1386a^3} - \frac{r^5}{1890a})f^{(4)}], \quad (75)$$

$$g_4(r) = \sqrt{9}[(\frac{r^6}{99a^5} - \frac{r^4}{63a^3})f^{(1)} - (\frac{r^6}{99a^4} - \frac{r^4}{63a^2})f^{(2)} + (\frac{r^8}{2574a^5} + \frac{5r^6}{1386a^3} - \frac{2r^4}{315a})f^{(3)} - (\frac{r^8}{2574a^4} + \frac{r^6}{4158a^2} - \frac{r^4}{945})f^{(4)}], \quad (76)$$

We use the small r expansion for $r < r_l$ where r_l is the value of r where the magnitude of the difference between the values of g_l, computed from the two expressions above, is minimum. This occurs typically at a few tenths of a Bohr, where the differences between the two values of g_l are quite small, on the order of 1 part in 10^6. The values for $f^{(n)}$ are determined numerically using a 5-point interpolation formula.[34]

Alternatively, one can determine the g_l by numerical integration of Eq.(62). With this approach special care must be exercised when $r - a$ is small, i.e. where the slope of g_l is discontinuous. The difficulty is manifested by the peak in g_l at $r = a$ becoming increasingly sharp with incrasing accuracy of the numerical integration.

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